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A Theorem on Spin-Eigenfunctions

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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A THEOREM ON SPIN-EIGENFUNCTIONS

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ABSTRACT

A theorem is proved to the effect that a wave function for a set of N spins, which is a product of single-spin wave functions and which is an eigenstate of the square of the total spin $\vec{S}$, must be a state with the maximum possible value of $\vec{S}^2$ and of S_z, z being an arbitrary direction. This theorem has been applied in a separate work by the authors to show strikingly that the imposition of symmetry restrictions of a common type on an approximate wave function can lead to a very poor physical description.

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I INTRODUCTION

In a paper by the authors on Hartree-Fock (HF) theory, [Phys. Rev. 156, 1 (1967)], an analogy is drawn between the HF approximation to a ground eigenfunction of a Hamiltonian H representing a system of electrons, and the Hartree approximation to the ground eigenstate of a Hamiltonian H_s representing a system of spins. An example is then presented which shows strikingly that making symmetry-restrictions on one's already otherwise restricted wave function (a rather common procedure) can lead to an extremely poor description.

Namely, let H_s be an isotropic Heisenberg Hamiltonian $-\Sigma\, J_{ij}\, \vec{S}_i \cdot \vec{S}_j$ with exchange parameters J_{ij} chosen in such a way that the Hamiltonian represents an antiferromagnet. The $\vec{S}_i$ are the individual spin operators satisfying by definition $\vec{S}_i^{\,2} = S(S+1)$, independent of i. The Hamiltonian commutes with $\vec{S}^2$, where $\vec{S} = \Sigma_{i=1}^{N} \vec{s}_i$. The exact energy eigenstates can, therefore, be chosen to be eigenstates of $\vec{S}^2$ also, and it is often helpful in practice to require this when dealing with exact

eigenstates. This suggests (following others) that we impose the same requirement on the Hartree approximation to the wave function. The latter, by definition, is of product form $\Psi = \Pi_i \phi_i$, where ϕ_i is a single-spin state. Let us therefore require that Ψ be an eigenstate of $\vec{S}^2$. The problem then, in this restricted Hartree theory, is to determine a lowest energy product wave function Ψ that is an eigenstate of $\vec{S}^2$. (This is completely analogous to a type of restriction conventionally used in symmetry-restricted HF theory).

We then make use of a <u>theorem</u>: a product Ψ of spin-s spin functions which is an eigenfunction of $\vec{S}^2$ has maximum multiplicity and the component of $\vec{S}$ in some direction has the maximum possible value. According to this theorem, the only Ψ's of product form which are eigenstates of $\vec{S}^2$ are ferromagnetic (with maximum value of $\vec{S}^2$). Thus, the symmetry-restricted Hartree approximation is the worst possible approximation in the present example of a Heisenberg antiferromagnet.

In the paper on Hartree-Fock theory mentioned earlier, the above theorem was stated without proof; the purpose of the present note is to supply the required proof, which is given in the next section.

It may be of interest to the reader that the theorem seemed to us to be very probably true, and we expected to find a very

simple proof without difficulty. Unfortunately, we have had to be satisfied with the following lengthy proof.

II. STATEMENT AND PROOF OF THEOREM

We first state the theorem more precisely and then give the proof.

Theorem. Let $\Psi = \phi_1(1)\phi_2(2)\ldots\phi_N(N)$ be a product of spin functions ϕ_i such that $\vec{s}_1^{\,2}\,\phi_i(1) = s(s+1)\phi_i(1)$ and $\langle\phi_i|\phi_i\rangle = 1$ for $i = 1,2,\ldots,N$. If

$$\vec{S}^2\,\Psi = \sigma(\sigma+1)\Psi \tag{1}$$

where $\vec{S} = \sum_{i=1}^{N} \vec{s}_i$, then $\vec{s}_1\cdot\hat{z}\,\phi_i(1) = s\phi_i(1)$, $i = 1,2,\ldots,N$ for some unit vector $\hat{z}$, and hence $\sigma = Ns$.

Proof. Before giving the proof in detail we sketch an outline of it. We first prove the theorem for $N = 2$, since the proof for general N is relatively short and simple when based on the result for $N = 2$. The proof for $N = 2$ involves two parts depending on whether or not $\langle\phi_2|\vec{s}|\phi_2\rangle = 0$. The most lengthy argument by far concerns the $\langle\phi_2|\vec{s}|\phi_2\rangle = 0$ case.

It is convenient to define

$$Q \equiv \sum_{i<j} \vec{s}_i\cdot\vec{s}_j$$

$$= \frac{1}{2}\left[\vec{S}^2 - \sum_{i=1} \vec{s}_i^{\,2}\right] = \frac{1}{2}\left[\vec{S}^2 - Ns(s+1)\right]$$

and the eigenstate problem

$$Q\Psi = \lambda\Psi \tag{2}$$

equivalent to (1), where $\lambda = \frac{1}{2}[\sigma(\sigma+1) - Ns(s+1)]$.

Consider (2) first for N = 2.

$$\vec{s}_1 \cdot \vec{s}_2 \ \phi_1(1)\phi_2(2) = \lambda \ \phi_1(1)\phi_2(2) \tag{3}$$

Take the scalar product with $\phi_2(2)$ to obtain

$$\vec{s}_1 \cdot \vec{\sigma}_2 \ \phi_1(1) = \lambda \ \phi_1(1) \tag{4}$$

where

$$\vec{\sigma}_i \equiv \langle\phi_i|\vec{s}|\phi_i\rangle \tag{5}$$

There are two cases to consider: (a) $\vec{\sigma}_2 \neq 0$ and (b) $\vec{\sigma}_2 = 0$.

(a) $\vec{\sigma}_2 \neq 0$

From (4), $\phi_1(1)$ is an eigenfunction $\chi_m(1)$ of $\vec{s}_1 \cdot \hat{\sigma}_2$

$$\vec{s}_1 \cdot \hat{\sigma}_2 \ \chi_m(1) = m \ \chi_m(1) \tag{6}$$

Expand $\phi_2(2)$ in terms of the χ_m

$$\phi_2 = \sum_{m'} b_{m'} \chi_{m'} \tag{7}$$

and substitute into (3) using

$$\vec{s}_1 \cdot \vec{s}_2 = s_{1z} s_{2z} + \frac{1}{2} s_{1+} \, s_{2-} + \frac{1}{2} s_{1-} \, s_{2+} \tag{8}$$

where $s_\pm = s_x \pm i s_y$. Obtain, using

$$s_\pm \, \chi_m = g_{\pm m} \, \chi_{m\pm 1} \tag{9}$$

where $g_m \equiv [(s-m)(s+m+1)]^{1/2} = g_{-m-1}$

$$m \sum_{m'} m' \, b_{m'} \, \chi_m(1) \chi_{m'}(2) + \frac{1}{2} g_m \, \chi_{m+1}(1) \sum_{m'} g_{-m'} \, b_{m'} \, \chi_{m'-1}(2)$$

$$+ \frac{1}{2} g_{-m} \, \chi_{m-1}(1) \sum_{m'} g_{m'} \, b_{m'} \, \chi_{m'+1}(2) = \lambda \, \chi_m(1) \sum_{m'} b_{m'} \, \chi_{m'}(2) \tag{10}$$

Take the scalar product with $\chi_m(1) \, \chi_{m'}(2)$, obtaining thereby

$$(mm' - \lambda) b_{m'} = 0 \tag{11}$$

This implies $b_{m'} = \delta_{m',\bar{m}}$ for some $\bar{m}$, $-s < \bar{m} < s$, and consequently $\lambda = m\bar{m}$. Substituting into (10) then yields

$$m\bar{m} \, \chi_m(1) \, \chi_{\bar{m}}(2) + \frac{1}{2} g_m \, g_{-\bar{m}} \, \chi_{m+1}(1) \, \chi_{\bar{m}-1}(2)$$

$$+ \frac{1}{2} g_{-m} \, g_{\bar{m}} \, \chi_{m-1}(1) \, \chi_{\bar{m}+1}(2) = m\bar{m} \, \chi_m(1) \, \chi_{\bar{m}}(2) \tag{12}$$

from which we conclude that

$$g_m \, g_{-\bar{m}} = 0 \tag{13a}$$

$$g_{-m} \, g_{\bar{m}} = 0 \tag{13b}$$

Equations (13) require either $g_m = g_{\bar{m}} = 0$ and hence $m = \bar{m} = s$, or $g_{-\bar{m}} = g_{-m} = 0$ and hence $m = \bar{m} = -s$. Thus, we conclude that when $\vec{\sigma}_2 \neq 0$, (3) has only solutions of the type

$$\phi_i = \chi_s \qquad i = 1,2 \tag{14}$$

where $\vec{s}_1 \cdot \hat{z}\, \chi_s(1) = s\, \chi_s(1)$ with $\hat{z}$ some unit vector.

<u>For an alternate proof</u> we note: once we know $\phi_1 = \chi_m$, then we know immediately that the only possible product eigenfunctions of $\vec{S}^2$ of the form $\chi_m(1)\phi_2(2)$ are just $\chi_s(1)\chi_s(2)$ and $\chi_{-s}(1)\chi_{-s}(2)$.

(b) $\vec{\sigma}_2 = 0$

In this case $\lambda = 0$ (excluding the physically uninteresting $\Psi = 0$ case) and (3) reduces to

$$\vec{s}_1 \cdot \vec{s}_2 \, \phi_1(1)\phi_2(2) = 0 \tag{15}$$

Choosing an arbitrary z-axis we expand ϕ_1 and ϕ_2

$$\phi_1 = \sum_m a_m \chi_m \tag{16a}$$

$$\phi_2 = \sum_{m'} b_{m'} \chi_{m'} \tag{16b}$$

where

$$\hat{s}\cdot\hat{z}\, \chi_m = m\, \chi_m \qquad -s < m < s \tag{17}$$

Then, (15) becomes, on using (8) and (16),

$$\sum_{mm'} \Big\{ mm'\, a_m\, b_{m'}\, \chi_m(1)\chi_{m'}(2) + \frac{1}{2}\, g_m\, g_{-m'}\, a_m\, b_{m'}\, \chi_{m+1}(1)\chi_{m'-1}(2)$$

$$+ \frac{1}{2}\, g_{-m}\, g_{m'}\, a_m\, b_{m'}\, \chi_{m-1}(1)\chi_{m+1}(2) \Big\} = 0 \tag{18}$$

Taking the scalar product with $\chi_m(1)\chi_{m'}(2)$ then gives

$$mm'\, a_m\, b_{m'} + \frac{1}{2}\, g_{m-1}\, g_{m'}\, a_{m-1}\, b_{m'+1} + \frac{1}{2}\, g_m\, g_{m'-1}\, a_{m+1}\, b_{m'-1} = 0 \tag{19}$$

Because (15) is symmetric with respect to interchange of 1 and 2, all consequences of (19) hold as well when a and b are interchanged.

Consider possible solutions of the set of $(2s+1)^2$ equations (19).

$$m = m' = s(\neq 0) \not\Rightarrow \qquad a_s b_s = 0$$

<u>CASE 1</u> $\quad b_s \neq 0 \not\Rightarrow a_s = 0$

With $m' = s$, (19) reduces to

$$ms\ a_m\ b_s + \frac{1}{2}\, g_m\ g_{s-1}\ a_{m+1}\ b_{s-1} = 0 \qquad (20)$$

This implies $a_m = 0$, $m = s - 1, s - 2, \ldots, 1$ whether or not $b_{s-1} = 0$. With $m = 1$, (19) then becomes

$$\frac{1}{2}\, g_o\ g_{m'}\ a_o\ b_{m'+1} = 0 \qquad (21)$$

and with $m' = s - 1$ this becomes $g_o g_{s-1} a_o b_s = 0$ which implies $a_o = 0$. Further use of (20) then implies $a_m = 0$, $m = -1, -2, \ldots, -s$. We therefore conclude for CASE 1 that there is <u>no</u> <u>solution</u> with $b_s \neq 0$, $a_s = 0$. Naturally, we next ask if, with $a_s = 0$, there is a solution of (19) with $b_s = 0$ and $b_{s-1} \neq 0$. If not, we then ask if there is a solution with $b_s = b_{s-1} = 0$, $b_{s-2} \neq 0$. And so on.

<u>CASE 2</u>

We shall proceed by treating the general case: we show that there is <u>no</u> <u>solution</u> of (19) with $b_s = b_{s-1} = \cdots = b_{s-k+1} = 0$ and $b_{s-k} \neq 0$, $k = 1, 2, \ldots, 2s$. To prove this we

suppose the contrary to be true. With $m' = s-k$, (19) becomes

$$m(s-k)a_m b_{s-k} + \frac{1}{2} g_{m-1} g_{s-k} a_{m-1} b_{s-k+1} + \frac{1}{2} g_m g_{s-k-1} a_{m+1} b_{s-k-1} = 0 \tag{22}$$

where now $b_{s-k+1} = 0$.

<u>CASE 2.1</u> $k \neq s$, $k \neq 2s$. The argument is similar to that of CASE 1. Now (22) with $m = s \Rightarrow \quad a_s = 0$, then

" $m = s - 1 \Rightarrow a_{s-1} = 0$, then

" $m = 1 \Rightarrow \quad a_1 = 0$.

Thus, (22) implies $a_m = 0$, $m = s, s - 1, \ldots, 1$. With $m' = 1$ in (19) we again obtain (20) which, with $m' + 1 = s - k$, reduces to

$$g_o g_{s-k-1} a_o b_{s-k} = 0 \tag{23}$$

which implies

$$a_o = 0$$

Then, (22) with $m = -1,-2,\ldots,-s \Rightarrow a_m = 0$, $m = -1,-2,\ldots,-s$. Thus, all the $a_m = 0$ and NO SOLUTION is possible in case 2.1.

<u>CASE 2.2</u> $k = s$

(19) with $m' = 1$ becomes in this case

$$\frac{1}{2} g_m g_o \; a_{m+1} \; b_o = 0 \tag{24}$$

which $\Rightarrow$ $a_m = 0$, $m = s, s - 1, \ldots, -s + 1$. Then (19) with $m = -s + 1 \Rightarrow$ ...

$$\frac{1}{2} g_{-s} g_{m'} \, a_{-s} \, b_{m'+1} = 0 \qquad (25)$$

With $m' = -1$ this gives $g_{-s} g_{-1} a_{-s} b_o = 0$ which $\Rightarrow$ $a_{-s} = 0$. Thus, all $a_m = 0$ in case 2.2 and there is no solution.

<u>CASE 2.3</u> $k = 2s$

(19) with $m' = -s + 1$ in this case $\Rightarrow$

$$g_m g_{-s} \, a_{m+1} b_{-s} = 0 \qquad (26)$$

With $m = s - 1, s - 2, \ldots, -s$, this $\Rightarrow$ $a_m = 0$, $m = s, s - 1, \ldots, -s + 1$.

(19) with $m' = -s$ then gives

$$- ms \, a_m b_{-s} = 0 \qquad (27)$$

with $m = -s$ this $\Rightarrow$ $a_{-s} = 0$.

Thus, all $a_m = 0$ in case 2.3, and there is no solution. This exhausts all possibilities. Thus, we conclude, there is no non-zero solution of (19). In other words, the only solution of (15) is $\phi_1 \phi_2 = 0$, which is of no physical interest.

To <u>summarize</u> the results proved so far, which are all for $N = 2$: We have proved that Eq. (3) has no solution with $\Psi \neq 0$ when $\lambda = 0$. Since from Eq. (4) we have that $\vec{\sigma}_2 = 0$ implies

$\lambda = 0$ if $\Psi \neq 0$, the only solutions with $\Psi \neq 0$ occur for $\vec{\sigma}_2 \neq 0$. These are given by (14).

<u>For General N:</u>

Take the scalar product of (2) with $\phi_3(3)\phi_4(4)\ldots\phi_N(N)$ and obtain

$$\left[\vec{s}_1\cdot\vec{s}_2 + \sum_{k>2}\vec{\sigma}_k\cdot(\vec{s}_1+\vec{s}_2) + \sum_{k>j>2}\vec{\sigma}_j\cdot\vec{\sigma}_k\right]\phi_1(1)\phi_2(2) = \lambda\;\phi_1(1)\phi_2(2) \tag{28}$$

where again $\vec{\sigma}_j \equiv \langle\phi_j|\vec{s}|\phi_j\rangle$.

As for N = 2, we consider two cases: (a) $\sum_{k>2}\vec{\sigma}_k \neq 0$ and (b) $\sum_{k>2}\vec{\sigma}_k = 0$. Let $\vec{\Sigma}_{12} \equiv \sum_{k>2}\vec{\sigma}_k$. If $\vec{\Sigma}_{12} = 0$, the eigenfunction in (28) is well known to be $\chi_s(1)\chi_s(2)$ the quantization axis being parallel or antiparallel to $\vec{\Sigma}_{12}$. If $\vec{\Sigma}_{12} = 0$, (28) reduces to (3), in which λ is replaced by $\lambda - \sum_{k>j>2}\vec{\sigma}_j\cdot\vec{\sigma}_k$, so that again the eigenfunction of (28) is $\chi_s(1)\chi_s(2)$ but with quantization axis undetermined.

If next we repeat this development with 1 and 2 replaced by i and j we obtain instead of (28)

$$\left[\vec{s}_i\cdot\vec{s}_j + \vec{\Sigma}_{ij}\cdot(\vec{s}_i+\vec{s}_j) + \sum_{\substack{k>\ell\\ \neq i,j}}\vec{\sigma}_k\cdot\vec{\sigma}_\ell\right]\phi_i(i)\phi_j(j) = \lambda\;\phi_i(i)\phi_j(j) \tag{29}$$

with

$$\vec{\Sigma}_{ij} \equiv \sum_{\substack{k=1 \\ k \neq i,j}}^{N} \vec{\sigma}_k \tag{30}$$

This, of course, reduces to (28) when $i = 1$ and $j = 2$. The eigenfunctions, determined as for (28), are $\chi_s(i)\chi_s(j)$ where the quantization axis of χ_s is arbitrary if $\vec{\Sigma}_{ij} = 0$ and along the axis of $\vec{\Sigma}_{ij}$ if $\vec{\Sigma}_{ij} \neq 0$. Now let $i = 1$, and let j run from 2 to N. Then, we see that we must have $\phi_j = \chi_s$ for all j, with a single quantization axis, which is not specified. This is a consistent solution, since $\vec{\Sigma}_{ij} = \vec{\Sigma} = (N-2)s\hat{z}$ for all pairs i,j with $\hat{z}$ the quantization axis, a consequence of $\vec{\sigma}_i = \vec{\sigma} = \langle\chi_s|\vec{s}|\chi_s\rangle = s\hat{z}$, independent of i. Finally, we have

$$\lambda = \sum_{i<j} \vec{\sigma}_i \cdot \vec{\sigma}_j = \frac{N(N-1)}{2} s^2$$

and hence from (2), $\sigma = Ns$.

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13. ABSTRACT

A theorem is proved to the effect that a wave function for a set of N spins, which is a product of single-spin wave functions and which is an eigenstate of the square of the total spin $\vec{S}$, must be a state with the maximum possible value of $\vec{S}^2$ and of S_z, z being an arbitrary direction. This theorem has been applied in a separate work by the authors to show strikingly that the imposition of symmetry restrictions of a common type on an approximate wave function can lead to a very poor physical description.

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